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(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

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TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

FL1049

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/485559

INTERNATIONAL APPLICATION NO.

PCT/US98/16689

INTERNATIONAL FILING DATE

12 AUGUST 1998 (12.08.98)

PRIORITY DATE CLAIMED

12 AUGUST 1997 (12.08.97)

TITLE OF INVENTION

PURIFICATION OF DIFLUOROMETHANE BY EXTRACTIVE DISTILLATION

APPLICANT(S) FOR DO/EO/US

BOEHMER, Sara W., et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☒ A change of power of attorney and/or address letter.
18. ☒ Certificate of Mailing by Express Mail
19. ☐ Other items or information:

17. General Power of Attorney

18. Express Mailing Label No.: EJ23661642US

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <div style="font-size: 24pt; font-weight: bold; text-align: center;">09/485559</div>	INTERNATIONAL APPLICATION NO. <div style="font-weight: bold; text-align: center;">PCT/US98/16689</div>	ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold; text-align: center;">FL1049</div>			
20. The following fees are submitted:. BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <div style="margin-left: 20px;"> <input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO \$840.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00 <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00 <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO \$970.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$96.00 </div> <div style="text-align: center; margin-top: 10px;"> ENTER APPROPRIATE BASIC FEE AMOUNT = </div>		<div style="background-color: #f0f0f0; padding: 5px; font-weight: bold;">CALCULATIONS PTO USE ONLY</div>			
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30		<div style="border: 1px solid black; padding: 5px; text-align: center;">\$840.00</div> <div style="border: 1px solid black; padding: 5px; text-align: center;">\$0.00</div>			
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	11 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$840.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).			<input type="checkbox"/>	\$0.00	
SUBTOTAL =				\$840.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30			+	\$0.00	
TOTAL NATIONAL FEE =				\$840.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).			<input checked="" type="checkbox"/>	\$40.00	
TOTAL FEES ENCLOSED =				\$880.00	
				Amount to be: refunded	\$
				charged	\$

☐ A check in the amount of _____ to cover the above fees is enclosed.

☒ Please charge my Deposit Account No. **04-1928** in the amount of **\$880.00** to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **04-1928** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE CRAIG H. EVANS
REG. NO. 31,825 FOR
SHIPLEY, James E.

NAME _____

32,003

REGISTRATION NUMBER

11 February 2000

DATE _____

TITLE
PURIFICATION OF DIFLUOROMETHANE BY EXTRACTIVE
DISTILLATION

5 **CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims the priority benefit of U.S. Provisional Application 60/055502, filed August 12, 1997.

10 **FIELD OF THE INVENTION**

The present invention relates to extractive distillation processes for purifying difluoromethane (CF_2H_2 , HFC-32).

BACKGROUND OF THE INVENTION

15 New regulations have been established to protect the stratospheric ozone layer from possible damage by chlorofluorocarbons (CFCs). Highly purified HFC-32 is a hydrofluorocarbon (HFC) that is valuable as an etchant gas in plasma etching of materials used in the fabrication of semiconductor devices.

20 HFC-32 may be prepared by allowing methylene chloride (CCl_2H_2) to react with hydrogen fluoride (HF) in the presence of an oxidized metal catalyst of metals such as chromium, antimony, and tantalum. HFC-32 may also be co-produced with HFCs such as pentafluoroethane ($\text{CF}_3\text{CF}_2\text{H}$, HFC-125) by such metal mediated processes in which an HFC-125 precursor compound such as tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$) is utilized. The HFC-32 reaction product
25 obtained from such processes may contain one or more of HFC-125, unreacted methylene chloride and HF, byproduct hydrogen chloride (HCl), and small amounts of organic byproducts such as 1,1,1-trifluoroethane (CF_3CH_3 , HFC-143a), dichlorodifluoromethane (CCl_2F_2 , CFC-12), chloropentafluoroethane (CClF_2CF_3 , CFC-115), methyl chloride (CH_3Cl , HCC-40), methyl fluoride (CH_3F , HFC-41), trifluoromethane (CF_3H , HFC-23), chlorodifluoromethane (CHClF_2 ,
30 HCFC-22), and 1,1-difluoroethane (CF_2HCH_3 , HFC-152a). The presence of even trace amounts of such impurities in HFC-32 can be undesirable in the utilization of HFC-32 as an etchant gas in plasma processes employed in the semiconductor industry.

35 Casey et al., in PCT publication WO9703936 disclose processes for separation of HFC-32 and HFC-125 by azeotropic distillation of a low boiling HFC-32/HFC-125 azeotrope, separation of a mixture of HFC-32 and CFC-115 by azeotropic distillation of a low boiling HFC-32/CFC-115 azeotrope, separation of

a mixture of HFC-32 and HFC-125 by extractive distillation employing methylene chloride as extractive agent, and separation of a mixture of HFC-32 and HFC-143a by employing CFC-115 as extractive agent.

Takahashi Reiji et al., in Japanese patent application JP 07291878, describe a process for the removal of HFC-143a, HFC-125, and methyl chloride from HFC-32 by extractive distillation. This process is characterized by employing at least one of 1,1-dichloro-1-fluoroethane (CCl_2FCH_3 , HCFC-141b), dichloropentafluoropropane, trichlorotrifluoroethane, and 2,2-dichloro-1,1,1-trifluoroethane (CHCl_2CF_3 , HCFC-123) as extractive agent. Using such CFC extractive agents is relatively expensive, and regulations concerning protection of the stratospheric ozone layer will cause CFCs to be phased out as commercial products thereby making CFCs unavailable or uneconomical for such a process.

The present invention solves problems associated with conventional purification methods and provides lower cost and more economical processes for separating HFC-32 from mixtures comprising HFC-32 and at least one halocarbon selected from HFC-143a, CFC-12, HFC-125, and CFC-115.

SUMMARY OF THE INVENTION

The present invention comprises a process for separating difluoromethane (HFC-32) from at least one halocarbon of a first mixture comprising difluoromethane (HFC-32) and halocarbon selected from the group consisting of chlorodifluoromethane (CFC-12), 1,1,1-trifluoroethane (HFC-143a), chloropentafluoroethane (CFC-115), and pentafluoroethane (HFC-125), comprising the steps of:

contacting the first mixture with an extractive agent selected from the group consisting of:

hydrocarbon extractive agents comprising hydrocarbons having from 5 to 9 carbon atoms and having a normal boiling point greater than about 30°C and less than about 155°C ,

oxygen-containing extractive agents comprising alcohols having a normal boiling point greater than about 60°C and less than about 100°C and represented by the formula $\text{C}_x\text{H}_{2x+1}\text{OH}$, wherein x is from 1 to 3, and ketones having a normal boiling point greater than about 50°C and less than about 110°C and represented by the formula $\text{C}_y\text{H}_{2y+1}\text{COC}_z\text{H}_{2z+1}$, wherein y and z are 1 or greater and $y+z$ is at most 5, and

chlorocarbon extractive agents comprising chlorocarbons having a normal boiling point greater than about 39°C and less than about 150°C

and represented by the formula $C_sH_{2s+2-t}Cl_t$, wherein s is 1 or 2 and t is from 2 to 4 to form a second mixture,

separating difluoromethane (HFC-32) from at least one halocarbon of the second mixture by extractively distilling the second mixture, and

5 recovering difluoromethane (HFC-32) substantially free of at least one halocarbon, with the proviso that when the halocarbon is pentafluoroethane (HFC-125), the chlorocarbon extractive agent may not be methylene chloride.

BRIEF DESCRIPTION OF THE DRAWINGS

10 Figure 1.- FIG.1 is a schematic diagram of an extractive distillation system that can be used for practicing an aspect of the present process.

DETAILED DESCRIPTION

HFC-32 is commonly synthesized by fluorination of methylene chloride
15 by a process wherein methylene chloride is allowed to react with hydrogen fluoride in the presence of a metal catalyst. HFC-32 so produced can contain a variety of impurities such as HCl, halocarbons such as HFC-143a and CFC-12, as well as unreacted methylene chloride and HF, among others. HFC-32 may also be co-produced with HFCs such as HFC-125 by such metal mediated processes in
20 which an HFC-125 precursor compound such as tetrachloroethylene ($CCl_2=CCl_2$) is utilized. In the event of such HFC-32/HFC-125 co-production, HFC-32 product may additionally contain HFC-125 and HFC-125 byproducts such as CFC-115. While most of the process impurities can be removed by conventional distillation, the halocarbons CFC-12, HFC-143a, CFC-115, and HFC-125 are difficult if not
25 impossible to remove by conventional distillation methods. This difficulty is due to the fact that CFC-12, HFC-143a, CFC-115, and HFC-125 form known azeotropes with HFC-32.

Halocarbon impurities of the present invention refers to at least one halocarbon selected from the group consisting of CFC-12, HFC-143a, CFC-115,
30 and HFC-125. In their separate and pure states, HFC-32 and the halocarbon impurities have atmospheric boiling points of about -52°C (HFC-32), -48°C (HFC-125), -47°C (HFC-143a), -39°C (CFC-115), and -30° (CFC-12). However, a mixture comprising at least one such halocarbon and HFC-32 exhibits non-ideal vapor-liquid behavior such that the relative volatility of HFC-32 and halocarbon is
35 very near 1.0. Conventional distillation procedures are incapable of efficiently separating HFC-32 from these halocarbons in instances where the relative volatility of HFC-32 and halocarbon is very near 1.0. The term conventional

distillation refers to the practice where only the relative volatility of the components of a mixture to be separated is used to separate the components.

To determine the relative volatility of HFC-32 and halocarbon, a method known as the PTx method was used. Use of the PTx method is described in detail in "Phase Equilibrium in Process Design," Wiley-Interscience Publisher, 1970, written by Harold R. Null, pages 124 through 126, hereby incorporated by reference. In the PTx method, the total absolute pressure in a cell of known volume is measured at a constant temperature for various known binary compositions of HFC-32 and halocarbon. These total pressure measurements are converted into equilibrium vapor and liquid compositions by employing an activity coefficient equation model such as the Non-Random, Two Liquid (NRTL) equation, which represents liquid phase non-idealities. Use of an activity coefficient equation such as the NRTL equation, is described in "The Properties of Gases and Liquids," 4th edition, published by McGraw Hill, written by Reid, Prausnitz and Poling, pages 241 through 387; and in "Phase Equilibria in Chemical Engineering," published in 1985 by Butterworth Publishers, written by Stanley M. Walas, pages 165 through 244. Both aforementioned references are hereby incorporated by reference. Without wishing to be bound by theory, it is believed that the NRTL equation can sufficiently predict the relative volatilities of mixtures comprising HFC-32 and the halocarbon impurities of the present invention.

The results of PTx measurements and the above calculations indicate that the relative volatilities of HFC-32 and halocarbon are equal to 1 for given compositions of HFC-32 and halocarbon over a range of temperatures. Relative volatilities of 1 in a mixture indicate the formation of an azeotrope. The results of PTx measurements and the above calculations indicate that the composition of the azeotropes varies with temperature. Tables 1 through 4 show the results of these calculations, specifically, how the composition of the HFC-32/halocarbon azeotropes varies with temperature. Because of the formation of azeotropes, it is difficult, if not impossible, to completely separate HFC-32 from halocarbon by conventional distillation techniques at temperatures and pressures within the ranges shown in Tables 1 through 4.

By azeotrope or azeotropic composition is meant a substantially constant boiling liquid mixture of two or more substances that behaves as a single substance. One way to characterize an azeotropic composition or mixture is that the vapor produced by partial evaporation or distillation of the liquid has substantially the same composition as the liquid from which it was evaporated or

Table 1 - Variation of the HFC-32/CFC-12 Azeotropic Composition with Temperature

Pressure/composition measurements were taken at 0°C and 40 °C and extrapolated over the temperature range using the aforementioned calculations.

5

Temp. (°C)	CFC-12 Mole Fraction, Liquid Phase	CFC-12 Mole Fraction, Vapor Phase	HFC-32 Mole Fraction, Liquid Phase	HFC-32 Mole Fraction, Vapor Phase	Vapor Pressure (psia)	Relative Volatility HFC-32/CFC-12
-80.0	0.1771	0.1771	0.8229	0.8229	3.0	1.000
-60.0	0.1802	0.1802	0.8198	0.8198	10.3	1.000
-40.0	0.1757	0.1757	0.8243	0.8243	27.6	1.000
-20.0	0.1647	0.1647	0.8353	0.8353	62.1	1.000
0.0	0.1480	0.1480	0.8520	0.8520	122.5	1.000
10.0	0.1376	0.1376	0.8624	0.8624	165.6	1.000
20.0	0.1255	0.1255	0.8745	0.8745	219.1	1.000
40.0	0.0946	0.0946	0.9054	0.9054	363.9	1.000
50.0	0.0736	0.0736	0.9265	0.9265	458.9	1.000
55.0	0.0602	0.0602	0.9398	0.9398	513.0	1.000

Table 2 - Variation of the HFC-32/HFC-143a Azeotropic Composition with Temperature

Pressure/composition measurements were taken at -17°C and 40 °C and extrapolated over the temperature range using the aforementioned calculations.

10

Temp. (°C)	HFC-143a Mole Fraction, Liquid Phase	HFC-143a Mole Fraction, Vapor Phase	HFC-32 Mole Fraction, Liquid Phase	HFC-32 Mole Fraction, Vapor Phase	Vapor Pressure (psia)	Relative Volatility HFC-32/HFC-143a
-80.0	0.2830	0.2830	0.7170	0.7170	2.9	1.000
-60.0	0.2334	0.2334	0.7666	0.7666	9.7	1.000
-50.0	0.2078	0.2078	0.7922	0.7922	16.4	1.000
-40.0	0.1818	0.1818	0.8182	0.8182	26.2	1.000
-20.0	0.1286	0.1286	0.8714	0.8714	59.3	1.000
0.0	0.0736	0.0736	0.9265	0.9265	118.2	1.000
10.0	0.0448	0.0448	0.9553	0.9553	160.7	1.000
20.0	0.0144	0.0144	0.9856	0.9856	213.9	1.000
23.0	0.0048	0.0048	0.9952	0.9952	232.2	1.000

Table 3 - Variation of the HFC-32/CFC-115 Azeotropic Composition with Temperature

Pressure/composition measurements were taken at 0°C and 39°C and extrapolated over the temperature range using the aforementioned calculations.

5

Temp. (°C)	CFC-115 Mole Fraction, Liquid Phase	CFC-115 Mole Fraction, Vapor Phase	HFC-32 Mole Fraction, Liquid Phase	HFC-32 Mole Fraction, Vapor Phase	Vapor Pressure (psia)	Relative Volatility HFC-32/CFC-115
-80.0	0.3040	0.3040	0.6960	0.6960	3.4	1.000
-60.0	0.3075	0.3075	0.6925	0.6925	11.7	1.000
-40.0	0.3023	0.3023	0.6977	0.6977	31.5	1.000
-20.0	0.2922	0.2922	0.7078	0.7078	70.6	1.000
0.0	0.2786	0.2786	0.7215	0.7215	138.3	1.000
10.0	0.2703	0.2703	0.7297	0.7297	185.9	1.000
20.0	0.2607	0.2607	0.7393	0.7393	244.3	1.000
40.0	0.2345	0.2345	0.7655	0.7655	398.4	1.000
60.0	0.1848	0.1848	0.8152	0.8152	606.3	1.000
80.0	0.0071	0.0071	0.9929	0.9929	866.1	1.000

Table 4 - Variation of the HFC-32/HFC-125 Azeotropic Composition with Temperature

Pressure/composition measurements were taken at -38, -15, 15, and 44°C and extrapolated over the temperature range using the aforementioned calculations.

10

Temp. (°C)	HFC-125 Mole Fraction, Liquid Phase	HFC-125 Mole Fraction, Vapor Phase	HFC-32 Mole Fraction, Liquid Phase	HFC-32 Mole Fraction, Vapor Phase	Vapor Pressure (psia)	Relative Volatility HFC-32/HFC-125
-80.0	0.1514	0.1514	0.8486	0.8486	2.8	1.000
-60.0	0.1359	0.1359	0.8641	0.8641	9.5	1.000
-40.0	0.1165	0.1165	0.8835	0.8835	25.9	1.000
-20.0	0.0952	0.0952	0.9048	0.9048	59.1	1.000
0.0	0.0746	0.0746	0.9254	0.9254	118.2	1.000
20.0	0.0592	0.0592	0.9408	0.9408	214.2	1.000
40.0	0.0590	0.0590	0.9410	0.9410	360.0	1.000
50.0	0.0737	0.0737	0.9263	0.9263	456.7	1.000

distilled, i.e., the mixture distills/refluxes without compositional change. Constant boiling compositions are characterized as azeotropic because they exhibit either a maximum or minimum boiling point relative to that of the pure components. Azeotropic compositions are also characterized by a minimum or a maximum in

15

the vapor pressure measurements relative to the vapor pressure of the pure components in a PTx cell as a function of composition at a constant temperature.

The fact that the HFC-32/halocarbon low-boiling (high pressure) azeotropic compositions vary depending on temperature and pressure provides a method of separating and partially purifying the HFC-32 from halocarbon. This method is known as azeotropic distillation and allows for partial separation of the azeotrope into its components within a distillation column. If the HFC-32/halocarbon azeotropic composition formed under one temperature/pressure is then distilled under a different temperature/pressure, the composition of the azeotrope will change such that one component, HFC-32 or halocarbon, is now in excess relative to the newly-formed azeotropic composition. By excess component is meant the component of an azeotropic composition which is in excess of the quantity of that component which is required for azeotropic formation at a given temperature and pressure. The newly formed azeotropic composition may then be distilled overhead while the excess component is recovered as column bottoms. For example, a distillation column can be operated at a temperature and pressure that causes the azeotropic composition to form. If the quantity of HFC-32 is relatively large in comparison to, for instance, HFC-143a, i.e. the concentration of HFC-32 is greater than that in the azeotropic composition, the HFC-32 can be removed in substantially pure form from the bottom of the column, while the azeotropic composition is removed from the top of the column.

The results of PTx measurements and the aforementioned calculations for HFC-32 and halocarbon in the presence of various extractive distillation agents are summarized in Tables 5 through 8. Shown are activity coefficients at 0 °C for HFC-32/CFC-12 (Table 5), HFC-32/HFC-143a (Table 6), HFC-32/CFC-115 (Table 7) and HFC-32/HFC-125 (Table 8) at infinite dilution in the listed extraction agent. Also shown are the ratios of HFC-32 activity coefficient to halocarbon activity coefficient (relative volatility). The ratio of the activity coefficient for HFC-32 at infinite dilution in an extractive agent relative to the activity coefficient of halocarbon at infinite dilution in the proposed extractive agent is the relative volatility of HFC-32 and halocarbon in the presence of the extractive agent.

Table 5 - Extractive Agents for HFC-32/CFC-12

			Infinite Dilution Activity Coefficients at 0°C		
Extractive Agent	Formula	NBP* (°C)	HFC-32	CFC-12	Ratio
n-Pentane	C ₅ H ₁₂	36.1	7.04	1.38	5.10
Methylcyclopentane	C ₆ H ₁₂	71.8	9.30	1.86	5.00
n-Hexane	C ₆ H ₁₄	68.7	7.25	1.48	4.90
Methanol	CH ₃ OH	64.6	3.89	10.82	0.36
Acetone	CH ₃ COCH ₃	56.3	0.77	3.23	0.24
Methylene Chloride	CH ₂ Cl ₂	39.8	2.77	4.04	0.69

*NBP = Normal Boiling Point (temperature at which vapor pressure is equal to 1 atmosphere)

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Table 6 - Extractive Agents for HFC-32/HFC-143a

			Infinite Dilution Activity Coefficients at 0°C		
Extractive Agent	Formula	NBP (°C)	HFC-32	HFC-143a	Ratio
n-Pentane	C ₅ H ₁₂	36.1	7.04	4.79	1.47
Cyclopentane	C ₅ H ₁₀	49.3	10.78	7.91	1.36
Methylcyclopentane	C ₆ H ₁₂	71.8	9.30	6.82	1.36
n-Hexane	C ₆ H ₁₄	68.7	7.25	5.22	1.39
Methanol	CH ₃ OH	64.6	3.89	7.71	0.50
Acetone	CH ₃ COCH ₃	56.3	0.77	1.78	0.43
Methylene Chloride	CH ₂ Cl ₂	39.8	2.77	4.82	0.57

Table 7 - Extractive Agents for HFC-32/CFC-115

			Infinite Dilution Activity Coefficients at 0°C		
Extractive Agent	Formula	NBP (°C)	HFC-32	CFC-115	Ratio
n-Pentane	C ₅ H ₁₂	36.1	7.04	6.61	1.07
Cyclopentane	C ₅ H ₁₀	49.3	10.78	5.95	1.81
n-Hexane	C ₆ H ₁₄	68.7	7.25	3.94	1.84
Methanol	CH ₃ OH	64.6	3.89	37.45	0.10
Acetone	CH ₃ COCH ₃	56.3	0.77	12.03	0.064
Methylene Chloride	CH ₂ Cl ₂	39.8	2.77	19.55	0.14

Table 8 - Extractive Agents for HFC-32/HFC-125

			Infinite Dilution Activity Coefficients at 0°C		
Extractive Agent	Formula	NBP (°C)	HFC-32	HFC-125	Ratio
n-Pentane	C ₅ H ₁₂	36.1	7.04	9.34	0.75
Cyclopentane	C ₅ H ₁₀	49.3	10.78	11.04	0.98
n-Hexane	C ₆ H ₁₄	68.7	7.25	6.65	1.09
Methanol	CH ₃ OH	64.6	3.89	3.94	0.99
Acetone	CH ₃ COCH ₃	56.3	0.77	0.87	0.89
Methylene Chloride	CH ₂ Cl ₂	39.8	2.77	9.53	0.29

The problems encountered upon conventional distillation of HFC-32/halocarbon, such as the need for taller columns, higher energy input, and lower resultant HFC-32 recovery, can be solved by practicing the present inventive extractive distillation process. By extractive distillation is meant a process in which an extractive agent is introduced at an upper feed point of a distillation column, whereas the mixture requiring separation is introduced at the same point or preferably, at a relatively lower feed point of the column. The substantially liquid extractive agent passes downwardly through trays or packing in the column and exits the column bottoms with one or more components of the mixture to be separated. While in the presence of the extractive agent, at least one of the components of an initial mixture to be separated becomes relatively more volatile compared to the other components of the mixture, with that more volatile

component of the initial mixture exiting the column overheads. Extractive distillation may be employed when the components of a mixture have relative volatilities that do not afford effective separation of the components by conventional distillation. In extractive distillation, an extractive agent is used which causes the relative volatilities of the components in a mixture to be altered such that the resultant relative volatilities, i.e., that of components of the mixture in the presence of the extractive agent, become sufficient to permit separation of the components by distillation techniques. The difficulty in applying this method is that there is no way of predicting which, if any, compound will be an effective extractive distillation agent for a given azeotropic composition.

The present inventors have discovered through experimentation that the relative volatility of compositions comprising HFC-32 and at least one of the halocarbons CFC-12, HFC-143a, CFC-115, and HFC-125 can be altered from 1.0 in the presence of extractive agents selected from: hydrocarbons having 5 to 9 carbon atoms and having a normal boiling point greater than about 30°C and less than about 155°C; alcohols having a normal boiling point greater than about 60°C and less than about 100°C and represented by the formula $C_xH_{2x+1}OH$, wherein x is from 1 to 3; ketones having a normal boiling point greater than about 50°C and less than about 110°C and represented by the formula $C_yH_{2y+1}COC_zH_{2z+1}$, wherein y and z are 1 or greater and y+z is at most 5; and chlorocarbons having a normal boiling point greater than about 39°C and less than about 150°C and represented by the formula $C_sH_{2s+2-t}Cl_t$, wherein s is 1 or 2 and t is from 2 to 4.

This discovery allows for separation of HFC-32 from a first mixture comprising HFC-32 and halocarbon by extractive distillation in the presence of an appropriate extractive agent. The appropriate extractive agent for a first mixture comprising HFC-32 and halocarbon is one which causes the relative volatility of the HFC-32 and halocarbon to be greater than 1.0, with the HFC-32 being more volatile, thus permitting HFC-32 to be removed from the top of the distillation zone. Alternately, the appropriate extractive agent for a first mixture comprising HFC-32 and halocarbon is one which causes the relative volatility of the HFC-32 and halocarbon to be less than 1.0, with the HFC-32 being less volatile, thus permitting halocarbon to be removed from the top of the distillation zone and HFC-32 to be removed from the bottom of the distillation zone together with the extractive agent. In order for an extractive agent to be effective in separating HFC-32 from halocarbon by extractive distillation, the relative volatility of the HFC-32 and halocarbon in the presence of the extractive agent must theoretically be greater than or less than about 1.0. For practical purposes it must generally be greater than about 1.1 or less than about 0.9. Normally, for commercially useful

separation of 32 and halocarbon to occur in the present extractive distillation process, this relative volatility will be greater than about 1.3 or less than about 0.5, and still more preferably it will be greater than about 2.0 or less than about 0.3.

When more than one halocarbon is present in a first mixture comprising HFC-32 and halocarbon, an effective extractive agent is one for which the relative volatility for each HFC-32/halocarbon pair of the first mixture satisfies the aforementioned relative volatility criteria in the same direction relative to 1.0. For instance, when CFC-12 and HFC-143a halocarbon impurities are both present in HFC-32 concurrently, an effective extractive agent is one for which the relative volatilities for both HFC-32/CFC-12 and HFC-32/HFC-143a are greater than 1.0.

The present inventors have discovered that at least one halocarbon selected from the group consisting of CFC-12, HFC-143a, CFC-115, and HFC-125 can be efficiently separated from HFC-32 by using an extractive distillation process with a hydrocarbon extractive agent comprising at least one linear, branched, or cyclic aliphatic hydrocarbon having a normal boiling point greater than about 30°C and less than about 155°C selected from the families of hydrocarbons known as pentanes, hexanes, heptanes, octanes, and nonanes. Hydrocarbon extractive agents with a normal boiling point between about 60°C and 110°C are especially useful. Preferred hydrocarbon extractive agents are n-pentane, cyclopentane, methylcyclopentane, n-hexane, cyclohexane and n-heptane. Hydrocarbon extractive agents used in the present invention are generally commercially available. Commercial grade hydrocarbons, such as Optima® grade Hexane available from Fisher Scientific, Pittsburgh, PA, USA, containing 2-methylpentane (0.2 volume %), 3-methylpentane (3.5%), n-hexane (85.4%), methylcyclopentane (10.9%), may be employed as hydrocarbon extractive agent in the process of the present invention. The extractive agent is chosen such that under the conditions of the extractive distillation, the extractive agent is not in the solid phase, i.e., the extractive agent does not freeze and form solid in the apparatus.

The present inventors have discovered that at least one halocarbon selected from the group consisting of CFC-12, HFC-143a, CFC-115, and HFC-125 can be efficiently separated from HFC-32 by using an extractive distillation process with an oxygen-containing extractive agent comprising: alcohols having a normal boiling point greater than about 60°C and less than about 100°C and represented by the formula $C_xH_{2x+1}OH$, wherein x is from 1 to 3; and ketones having a normal boiling point greater than about 50°C and less than about 110°C and represented by the formula $C_yH_{2y+1}COC_zH_{2z+1}$, wherein y and z are 1 or greater and y+z is at

most 5. Representative oxygen-containing extractive agents are methanol, ethanol, n-propanol, iso-propanol, propanone (acetone), and butanone.

The present inventors have discovered that at least one halocarbon selected from the group consisting of CFC-12, HFC-143a, CFC-115, and HFC-125 can be
 5 efficiently separated from HFC-32 by using an extractive distillation process with a chlorocarbon extractive agent comprising chlorocarbons having a normal boiling point greater than about 39°C and less than about 150°C and represented by the formula $C_sH_{2s+2-t}Cl_t$, wherein s is 1 or 2 and t is from 2 to 4. Representative
 10 chlorocarbon extractive agents are methylene chloride (CH_2Cl_2), chloroform (trichloromethane, $CHCl_3$), carbon tetrachloride (CCl_4), dichloroethane (CH_3CHCl_2 , CH_2ClCH_2Cl), trichloroethane (CH_3CCl_3 , $CHCl_2CH_2Cl$), and tetrachloroethane (CH_2ClCCl_3 , $CHCl_2CHCl_2$).

The extractive distillation processes of the present invention for separating HFC-32 from at least one halocarbon comprise the steps of:

- 15 a) contacting a HFC-32/halocarbon first mixture with an extractive agent to form a second mixture, and
- b) separating the HFC-32 from at least one halocarbon of the second mixture by extractively distilling the second mixture in an extractive distillation zone thereby recovering HFC-32 substantially free of at least one halocarbon:
 20 as an overhead product, and from the bottom of the zone a third mixture comprising the extractive agent and halocarbon for the embodiment of the present invention wherein the HFC-32 and halocarbon relative volatility is greater than 1.0, or
 as a bottoms product together with extractive agent, and as
 25 a third mixture an overhead product comprising halocarbon for the embodiment of the present invention wherein the HFC-32 and halocarbon relative volatility is less than 1.0.

In each of the aforementioned embodiments, the extractive agent is preferably recycled. For instance, for extractive agents causing a HFC-32 and
 30 halocarbon relative volatility greater than 1.0, extractive agent will be recovered from the extractive distillation step together with halocarbon, and may be further purified (e.g., by conventional distillation) and recycled to the contacting step. For extractive agents causing HFC-32 and halocarbon relative volatility less than 1.0, extractive agent will be recovered from the extractive distillation step together
 35 with HFC-32, and may be further purified (e.g., by conventional distillation) and recycled to the contacting step leaving HFC-32 substantially free of halocarbon.

By substantially free or substantially pure, it is meant that the HFC-32 product contains less than about 0.1 weight% halocarbon, and preferably less than

about 50 parts per million by weight (ppmw) of halocarbon. Higher purity HFC-32 for use as plasma etchant gas, e.g., containing 0.1 ppmw or less of halocarbon, may be produced by the present extractive distillation process by varying the extractant flow and distillation column dimensions.

5 While the present process may be used to purify a wide range of HFC-32 compositions containing one or more of the present halocarbons, it is preferred that the HFC-32 content be greater than about 90 mole% and that the halocarbon content be less than about 10 mole%. If desired, the aforementioned azeotropic distillation method can be used for reducing the initial quantity of
10 halocarbon and other impurities in the HFC-32 composition. That is, conventional distillation can be used for removing relatively large or bulk quantities of impurities from the first mixture which in turn is processed in accordance with the inventive process for separating HFC-32 from halocarbon.

Extractive distillation is typically performed by operating a
15 continuous distillation column, which comprises a multi-stage distillation column with two feed points. Extractive agent is introduced at a first feed point on the column which is located at the same height, more preferably above, a second feed point that is used for introducing the HFC-32/halocarbon mixture to be separated. The distillation column further comprises a reboiler and an overhead condenser
20 for returning reflux to the column.

In one embodiment of the present process, hydrocarbon extractive agent is introduced at an upper feed point of an extractive distillation column, whereas the first mixture requiring separation, e.g., comprising HFC-32 and halocarbon, is introduced at a relatively lower point in the column. The
25 hydrocarbon extractive agent passes downwardly through trays in the column and contacts the first mixture thereby forming a second mixture. While in the presence of the hydrocarbon extractive agent, HFC-32 is relatively more volatile than halocarbon, thereby causing substantially pure HFC-32 to exit the top of the column. HFC-32 exiting the top of the column can be condensed by reflux
30 condensers. At least a portion of this condensed stream can be returned to the top of the column as reflux, and the remainder recovered as substantially pure HFC-32 product. Hydrocarbon extractive agent, halocarbon, and other impurities comprise a third mixture that exits from the bottom of the column, which can then be passed to a stripper or distillation column for separation by using conventional
35 distillation or other known methods. The hydrocarbon extractive agent can be recycled to the extractive distillation column.

In another embodiment of the present process, oxygen-containing or chlorocarbon extractive agent is introduced at an upper feed point of an extractive

distillation column, whereas the first mixture requiring separation, e.g., comprising HFC-32 and halocarbon, is introduced at a relatively lower point in the column. The oxygen-containing or chlorocarbon extractive agent passes downwardly through trays in the column and contacts the first mixture thereby forming a second mixture. While in the presence of oxygen-containing or chlorocarbon extractive agent, halocarbons are relatively more volatile than HFC-32, thereby causing halocarbons to exit the top of the column. Oxygen-containing or chlorocarbon extractive agent and substantially pure HFC-32 comprise a third mixture that exits from the bottom of the column, which can in turn be passed to a stripper or distillation column for separation by using conventional distillation or other known methods. The oxygen-containing or chlorocarbon extractive agent can be recycled to the extractive distillation column.

The ratio of the material exiting the top of the extractive distillation column, which is then condensed and in turn returned to the column, to the amount of material that is removed as product is commonly referred to as the reflux ratio. The reflux ratio will define the physical characteristics of the extractive distillation column. In general, an increase in the reflux ratio will in turn cause an increase in the purity of the overhead stream (HFC-32 or halocarbon) by reducing or eliminating the quantity of extractive agent and other impurities in the overhead stream.

The specific conditions that can be used for practicing the invention depend upon a number of interrelated design parameters such as the diameter of the column, feed point location on the column, and the number of separation stages in the column, among other parameters. The operating pressure of the distillation system may range from about 15 to about 350 psia, normally about 50 to 300 psia. The temperature and heat transfer area of the overhead condenser is normally sufficient to substantially fully condense the overhead product, or is optionally sufficient to achieve the desired reflux ratio by partial condensation.

The effective amount of extractive agent can vary widely. In general, increasing the amount of extractive agent will increase the purity of the overhead HFC-32 or halocarbon stream. Typically, the ratio of extractive agent to HFC-32 ranges from about 1/1 to 10/1 on a weight basis; however, higher ratios can be employed.

The temperature that is employed at a given step in the inventive process may vary, as column operating temperature is a function of the pressure and design characteristics of the distillation column, e.g., the ratio of extractive agent to the first mixture.

The present inventive process can be better understood by reference to Figure 1. Figure 1 schematically illustrates a system which can be used for performing the embodiment of the present extractive distillation process wherein HFC-32 is separated from a first mixture comprising HFC-32 and halocarbon using a hydrocarbon extractive agent.

5 A first mixture comprising HFC-32 and halocarbon impurity is supplied via conduit 1 to extraction column 2. At least one liquid hydrocarbon extractive agent is supplied via conduit 3 to the extraction column 2, and introduced into column 2 at a location above the mixture 1. A second mixture
10 comprising the hydrocarbon extractive agent and halocarbon is removed from the bottom of column 2 and transported to steam heated reboiler 4. In some cases, reboiler 4 is attached to extractive column 2. The second mixture is supplied via conduit 5 to a feed tank 6. Supplemental liquid hydrocarbon extractive agent is also supplied to feed tank 6 via conduit 7 thereby forming a hydrocarbon
15 extractive agent recycle. A pump 8 transports the hydrocarbon extractive agent recycle to a stripping mixture column 9. Stripping column 9 separates the hydrocarbon extractive agent from other materials. Hydrocarbon extractive agent is removed from column 9 and supplied to a second steam heated reboiler 10. In some cases, the reboiler 10 is attached to column 9. Pump 11 transports the
20 hydrocarbon extractive agent from the reboiler 10 through a cold water chiller 12, and then to chiller 13. If necessary, excess quantities of hydrocarbon extractive agent can be purged prior to reaching chiller 12. Typically, chiller 13 is operated at a temperature of about -25°C. After exiting chiller 13, the hydrocarbon extractive agent is supplied via conduit 3 into extraction column 2.
25 Halocarbon exits from the top of stripping column 9 as an off gas, and is introduced into condenser 14, which is typically operated at a temperature of about -25°C. While under reflux conditions, pump 15 returns a portion of the halocarbon to the stripping column 9. The remaining portion of the halocarbon can be removed from the system via conduit 16.
30 An off gas of HFC-32 that is substantially free of halocarbon and other compounds is removed from extraction column 2. The HFC-32 is transported via conduit 17 to condenser 18. Condenser 18 is typically operated at a temperature of about -25°C. While under reflux conditions, pump 19 returns a portion of the HFC-32 to extraction column 2. The HFC-32 can be removed from
35 the system via conduit 20.

EXAMPLES

The following Examples are provided to illustrate certain aspects of the present invention, and do not limit the scope of the invention. In the following Examples, each column stage is based upon a 100% operational or performance efficiency. Differing column designs and operating conditions are employed using different extractive agents in order to maximize the performance of each distillation. In all examples, the total theoretical stages includes condenser and reboiler, with the condenser counted as stage No.1.

EXAMPLE 1

In this Example of the invention, a low boiler distillation column and an extractive distillation column were used to purify a feed stream composed of 10 lb/hr of crude HFC-32. The crude feed contained 0.00022 lb/hr of CFC-12, a CFC-12 concentration of 22 parts per million by weight (ppmw), and 0.00229 lb/hr of HFC-143a, a HFC-143a concentration of 229 ppmw. Other feed impurities were: 678 ppmw HFC-23 (CHF_3), 63 ppmw HFC-41 (CH_3F), 46 ppmw HCFC-22 (CHClF_2), 13 ppmw HCC-40 (CH_3Cl), 6 ppmw HFC-134a (CH_2FCF_3), 4 ppmw HFC-134 (CHF_2CHF_2), and 0.2 ppmw HFC-152a (CHF_2CH_3). The low boiler column was a packed column containing 23 theoretical stages. The crude feed stream was introduced at stage 12 of the low boiler column. The low boiler column condenser pressure was maintained at 190 psia. The distillate temperature was 15°C and the bottom column temperature was 16°C. The low boiler column boilup rate was set so as to give at least 40 lb/hr of internal reflux in the column (calculated based on condenser duty). The distillate takeoff rate was controlled at 0.5 lb/hr. Under these conditions, the low boiling impurities in the crude feed stream left the top of the low boiler column while the HFC-32 and its near boiling and high boiling impurities left with the bottoms stream. A sample of the bottoms stream indicated the following composition: 99.9785 wt% HFC-32, 172 ppmw HFC-143a, 25 ppmw HCC-40, 12 ppmw HCFC-22, 5 ppmw HFC-134a, and 1 ppmw HFC-134.

The extractive distillation column was a packed column containing 54 theoretical stages. The bottoms stream from the low boiler column was introduced at stage 33 of the extractive distillation column and n-hexane extractive agent was introduced at stage 13 at 150 lb/hr. The column condenser pressure was maintained at 84.7 psia. The distillate temperature was -9°C, and the bottom column temperature was 110°C. Under these operating conditions, the HFC-32 product left in the overhead stream from the column and the n-hexane containing HFC-143a exited in the bottom stream. The extractive agent flow rate was set so as to meet a composition of less than 25 ppmw of HFC-143a in the

overhead HFC-32 product. The column boilup rate of 28 lb/hr of steam to the reboiler was set so as to give sufficient reflux to meet a composition of less than 5 ppmw extractive agent in the HFC-32 overhead product. The distillate rate was controlled to recover 9 lb/hr of HFC-32 in the distillate overhead stream. The column diameter was chosen so as to have an F-factor of 0.59 or below. HFC-32 of 99.998 wt% purity was recovered with 99.89 % recovery of the HFC-32 fed to the extractive distillation column. The HFC-32 product contained 16 ppmw of HFC-143a, 1 ppmw of HCC-40, and 2 ppmw of n-hexane.

10 **EXAMPLE 2**

In this Example of the invention, a low boiler distillation column and an extractive distillation column were used to purify a feed stream composed of 20 lb/hr of crude HFC-32. The crude feed contained 0.00148 lb/hr of CFC-12, a CFC-12 concentration of 74 parts per million by weight (ppmw), and 0.00270 lb/hr of HFC-143a, a HFC-143a concentration of 135 ppmw. Other feed impurities were: 31 ppmw n-hexane (C_6H_{14}), 21 ppmw HCFC-22 ($CHClF_2$), 7 ppmw HCC-40 (CH_3Cl), 1 ppmw HFC-134a (CH_2FCF_3), and 1 ppmw CFC-13 ($CClF_3$). The low boiler column was a packed column containing 23 theoretical stages. The crude feed stream was introduced at stage 12 of the low boiler column. The low boiler column condenser pressure was maintained at 190 psia. The distillate temperature was 15°C and the bottom column temperature was 16°C. The low boiler column boilup rate was set so as to give at least 40 lb/hr of internal reflux in the column (calculated based on condenser duty). The distillate takeoff rate was controlled at 0.2 lb/hr. Under these conditions, the low boiling impurities in the crude feed stream left the top of the low boiler column while the HFC-32 and its near boiling and high boiling impurities left with the bottoms stream. A sample of the bottoms stream indicated the following composition: 99.9823 wt% HFC-32, 121 ppmw HFC-143a, 24 ppmw n-hexane, 20 ppmw HCFC-22, 7 ppmw HCC-40, and 5 ppmw CFC-12.

The extractive distillation column was a packed column containing 54 theoretical stages. The bottoms from the low boiler column was introduced at stage 33 of the extractive distillation column and the n-hexane extractive agent was introduced at stage 13 at 150 lb/hr. The column condenser pressure was maintained at 84.7 psia. The distillate temperature was -9°C, and the bottom column temperature was 120°C. Under these operating conditions, the HFC-32 product left in the overhead stream from the column and the n-hexane containing CFC-12 and HFC-143a exited in the bottom stream. The extractive agent flow rate was set so as to meet a composition of less than 40 ppmw of HFC-143a in the

overhead HFC-32 product. The column boilup rate of 28 lb/hr of steam to the reboiler was set so as to give sufficient reflux to meet a composition of less than 5 ppmw extractive agent in the HFC-32 overhead product. The distillate rate was controlled to recover 19.5 lb/hr of HFC-32 in the distillate overhead stream. The column diameter was chosen so as to have an F-factor of 0.59 or below. HFC-32 of 99.9964 wt% purity was recovered with 98.75 % recovery of HFC-32 fed to the extractive distillation column. The HFC-32 product contained 30 ppmw of HFC-143a and 6 ppmw of other unknown impurities; CFC-12 was below detectable limits in the product.

10

Examples 3-16 Comparative Examples 1-4

The following examples are calculated, theoretical examples employing the aforementioned NRTL interaction parameters. The examples are based on 1000 lb/hr of crude HFC-32 feed containing selected halocarbon impurities. No other impurities were considered to be present in the feed. Also included are calculated, theoretical Comparative Examples employing the aforementioned NRTL interaction parameters.

15

Table 9 - Comparative Examples - Distillation Using No Extractive Agent

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Process Feed (lb/hr)	1,000	1,000	1,000	1,000
HFC-32 (wt%)	99.99	99.99	99.96	99.0
<u>ppm</u> HFC-143a	100	100	100	0
CFC-12	0	0	100	5,000
CFC-115	0	0	100	5,000
HFC-125	0	0	100	0
Total # Column Stages	100	100	100	100
Process Stream Feed Stage #	50	50	50	50
Process Feed Temperature (°C)	-10	-10	-15	-15
Operating Pressure (psia)	84.7	84.7	84.7	84.7
Distillate Temperature (°C)	-9.9	-9.9	-10.1	-13.1
Bottoms Temperature (°C)	-8.9	-8.9	-8.9	-8.9
Q Condenser (pcu/hr)	-818,700	-221,500	-810,200	-622,300
Q Reboiler (pcu/hr)	819,100	221,700	812,600	624,700
Reflux Flow (lb/hr)	10,000	2,000	10,000	10,000
HFC-32 Purity (wt%)	99.9973	99.9973	99.992	99.9995
<u>ppm</u> CFC-12	-	-	0	5
HFC-143a	27	27	34	-
CFC-115	-	-	0	0
HFC-125	-	-	46	-
% of HFC-32 Feed Recovered	96.8	28.8	98.3	98.5

Table 10 - Removal of Halocarbon from HFC-32 using n-Hexane as Extractive Agent

	-Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Process Feed (lb/hr)	1,000	1,000	1,000	1,000	1,000	1,000
HFC-32 (wt%)	99.99	99.99	99.98	99.96	99.96	99.0
<u>ppm</u> HFC-143a	0	100	100	100	100	0
CFC-12	100	0	100	100	100	5,000
CFC-115	0	0	0	100	100	5,000
HFC-125	0	0	0	100	100	0
Total # Column Stages	47	69	69	69	69	69
Extractive Agent Feed Stage #	13	13	13	13	13	13
Process Stream Feed Stage #	35	52	52	52	52	52
Process Feed Temperature (°C)	-15	-15	-15	-15	-15	-15
Extractant feed Temperature (°C)	-15	-15	-15	-15	-15	-15
Operating Pressure (psia)	84.7	84.7	84.7	84.7	84.7	84.7
Distillate Temperature (°C)	-9.9	-9.9	-9.9	-9.9	-9.9	-9.9
Bottoms Temperature (°C)	129.9	138.3	138.3	138.6	139.0	138.2
Q Condenser (pcu/hr)	-136,200	-138,700	-138,700	-138,700	-138,700	-162,400
Q Reboiler (pcu/hr)	202,500	770,900	770,900	1,043,000	1,950,100	950,200
Reflux Flow (lb/hr)	670	700	700	700	700	1,000
Extractive Agent Flow (lb/hr)	760	7,000	7,000	10,000	20,000	8,730
HFC-32 Purity (wt%)	99.9994	99.9973	99.9973	99.9922	99.9964	99.9995
<u>ppm</u> CFC-12	5	-	0	0	0	0
HFC-143a	-	26	26	8	0	-
CFC-115	-	-	-	0	0	5
HFC-125	-	-	-	69	36	-
n-Hexane	1	1	1	1	1	0.1
% of HFC-32 Feed Recovered	99.8	99.8	99.8	99.8	99.8	99.8

Table 11 - Removal of CFC-12 and HFC-143a from HFC-32 using n-Pentane as Extractive Agent

	- Example 9	Example 10	Example 11
Process Feed (lb/hr)	1,000	1,000	1,000
HFC-32 (wt%)	99.99	99.99	99.98
<u>ppm</u> HFC-143a	0	100	100
CFC-12	100	0	100
Total # Column Stages	69	69	69
Extractive Agent Feed Stage #	36	36	36
Process Stream Feed Stage #	52	52	52
Process Feed Temperature (°C)	-15	-15	-15
Extractant feed Temperature (°C)	-15	-15	-15
Operating Pressure (psia)	84.7	84.7	84.7
Distillate Temperature (°C)	-9.9	-9.9	-9.9
Bottoms Temperature (°C)	99.4	100.5	100.5
Q Condenser (pcu/hr)	-440,900	-440,900	-440,900
Q Reboiler (pcu/hr)	526,300	795,800	795,800
Reflux Flow (lb/hr)	4,400	4,400	4,400
Extractive Agent Flow (lb/hr)	1,264	5,302	5,302
HFC-32 Purity (wt%)	99.9994	99.9974	99.9974
<u>ppm</u> CFC-12	5	-	0
HFC-143a	-	25	25
n-Pentane	1	1	1
% of HFC-32 Feed Recovered	99.8	99.8	99.8

Table 12 - Removal of Halocarbon from HFC-32 using Methanol, Methylene Chloride, and Acetone as Extractive Agents

	Example 12	Example 13	Example 14	Example 15	Example 16
Extractive Agent	Methanol	Methanol	Methylene Chloride	Acetone	Acetone
Process Feed (lb/hr)	1,000	1,000	1,000	1,000	1,000
HFC-32 (wt%)	99.96	99.96	99.96	99.96	99.96
ppm					
HFC-143a	100	100	100	100	100
CFC-12	100	100	100	100	100
CFC-115	100	100	100	100	100
HFC-125	100	100	100	100	100
Total # Column Stages	69	69	69	69	69
Extractive Agent Feed Stage #	10	10	10	10	10
Process Stream Feed Stage #	52	52	52	52	52
Process Feed Temperature (°C)	-15	-15	-15	-15	-15
Extractant feed Temperature (°C)	-15	-15	-15	-15	-15
Operating Pressure (psia)	84.7	84.7	84.7	84.7	84.7
Distillate Temperature (°C)	-11.1	-11.1	-10.9	-11.1	-11.1
Bottoms Temperature (°C)	61.8	90.8	36.1	90.0	104.3
Q Condenser (pcu/hr)	-38,900	-38,600	-38,700	-37,600	-37,500
Q Reboiler (pcu/hr)	541,000	1,421,900	204,500	647,300	1,383,700
Reflux Flow (lb/hr)	500	500	500	500	500
Extractive Agent Flow (lb/hr)	10,000	20,000	10,000	10,000	20,000
HFC-32 Purity (wt%)	99.982	99.986	99.982	99.9965	99.9989
ppm					
CFC-12	55	31	100	7	1
HFC-143a	22	5	79	25	9
CFC-115	0	0	0	0	0
HFC-125	100	100	2	3	1
% of HFC-32 Feed Recovered	99.8	99.8	99.8	99.8	99.8

WHAT IS CLAIMED IS:

1. A process for separating difluoromethane (HFC-32) from at least one halocarbon of a first mixture comprising difluoromethane (HFC-32) and
 5 halocarbon selected from the group consisting of chlorodifluoromethane (CFC-12), 1,1,1-trifluoroethane (HFC-143a), chloropentafluoroethane (CFC-115), and pentafluoroethane (HFC-125), comprising the steps of:
 contacting the first mixture with an extractive agent selected from the group consisting of:
 10 hydrocarbon extractive agents comprising hydrocarbons having from 5 to 9 carbon atoms and having a normal boiling point greater than about 30°C and less than about 155°C,
 oxygen-containing extractive agents comprising alcohols having a normal boiling point greater than about 60°C and less than about 100°C
 15 and represented by the formula $C_xH_{2x+1}OH$, wherein x is from 1 to 3, and ketones having a normal boiling point greater than about 50°C and less than about 110°C and represented by the formula $C_yH_{2y+1}COC_zH_{2z+1}$, wherein y and z are 1 or greater and y+z is at most 5, and
 chlorocarbon extractive agents comprising chlorocarbons having a
 20 normal boiling point greater than about 39°C and less than about 150°C and represented by the formula $C_sH_{2s+2-t}Cl_t$, wherein s is 1 or 2 and t is from 2 to 4 to form a second mixture,
 separating difluoromethane (HFC-32) from at least one halocarbon of the second mixture by extractively distilling the second mixture, and
 25 recovering difluoromethane (HFC-32) substantially free of at least one halocarbon, with the proviso that when the halocarbon is pentafluoroethane (HFC-125), the chlorocarbon extractive agent may not be methylene chloride.
2. The process of Claim 1 wherein the hydrocarbon extractive agent is
 30 selected from the group consisting of hydrocarbons having 5 to 7 carbon atoms and having a normal boiling point greater than about 30°C and less than about 110°C.
3. The process of Claim 2 wherein the hydrocarbon extractive agent is
 35 selected from the group consisting of n-pentane, 2-methylpentane, 3-methylpentane, cyclopentane, methylcyclopentane, n-hexane, cyclohexane and n-heptane.

4. The process of Claim 1 wherein the oxygen-containing extractive agent is selected from the group consisting of methanol, ethanol, propanol, isopropanol, propanone, and butanone.

5 5. The process of Claim 1 wherein the chlorocarbon extractive agent is methylene chloride.

6. The process of Claim 1 wherein the difluoromethane (HFC-32) recovered from the second mixture contains less than about 50 ppmw halocarbon.
10

7. The process of Claim 1 wherein the difluoromethane (HFC-32) recovered from the second mixture contains less than about 0.1 ppmw halocarbon.

8. The process of Claim 1 further comprising recycling at least a
15 portion of the extractive agent obtained from the extractive distillation of said separation step for use in preparation of the second mixture of said contacting step.

9. The process of Claim 1 wherein the extractive distillation is
20 performed at a pressure from about 15 to 350 psia.

10. The process of Claim 1 wherein the extractive distillation is performed using a reflux ratio of from about 1/1 to about 10/1.

25 11. The process of Claim 1 wherein the difluoromethane (HFC-32) and halocarbon of the first mixture are an azeotropic composition.

FIG. 1

The diagram illustrates a two-stage industrial process. Stage 1 on the left features a main unit (2) with an inlet (1) at the bottom and an outlet (17) at the top. Unit 2 is connected to a pump (19) and a storage tank (18). A side stream from unit 2 passes through a pump (13) and a storage tank (12) before entering a second pump (14). Stage 2 on the right features a main unit (9) with an inlet from unit 2 and an outlet (16) at the top. Unit 9 is connected to a pump (8) and a storage tank (6). A side stream from unit 9 passes through a pump (10) and a storage tank (11) before entering a second pump (14). The two pumps (14) are connected to a common outlet line (5) at the bottom, which leads to a final outlet (7) on the right. The entire system is enclosed within a boundary labeled 20.

FIG. 1

GENERAL POWER OF ATTORNEY
(Concerning Several International Patent Applications)

The undersigned, Howard J. Rudge, Senior Vice President and General Counsel of E. I. DU PONT DE NEMOURS AND COMPANY, 1007 Market Street, Wilmington, Delaware 19898 USA ("DuPont"), hereby confirms that the power to sign for DuPont has been granted to various individuals (as set forth in the attached excerpt from DuPont's Patent Board Rules of Procedure (January 1988), Appendix Section III.A.4), including the Chairman, Vice-Chairman, and those individuals who are Assistant Secretaries of the Patent Board. Currently these Assistant Secretaries are:

Alanson G. Bowen, Jr.	Miriam D. Meconnahey
Linda J. Davis	Dorothy W. Shafer
John E. Griffiths	Deborah A. Meginniss

In addition, the authority to act on behalf of DuPont before the competent International Authorities in connection with any and all international patent applications filed by it with the United States as Receiving Office and to make or receive payments on its behalf is hereby granted to:

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Floyd, Linda Axiemethy	33,692	Schaeffer, Andrew L.	33,605
Frank, George A.	27,636	Shafer, Robert J.	24,437
Fricke, Hilmar L.	22,384	Shay, Lucas K.	34,724
Golian, Andrew G.	25,293	Shiple, James E.	32,003
Gorman, Thomas W.	31,959	Siegell, Barbara C.	30,684
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Griffiths, John E.	32,647	Stevenson, Robert B.	26,039
Hamby, Jane O.	32,872	Strickland, Frederick D.	39,041
Hamby, William H.	31,521	Tessari, Joseph A.	32,177
Heiser, David E.	31,366	Tulloch, Rebecca W.	36,297
Hendrickson, John S.	30,847	Walker, P. Michael	32,602
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The undersigned ratifies fully all actions already taken by the above-named individuals in accordance with the authority granted hereby.

E. I. DU PONT DE NEMOURS AND COMPANY

By: Howard J. Rudge
Howard J. Rudge
Senior Vice President and General Counsel

Date: July 15, 1999

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DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PURIFICATION OF DIFLUOROMETHANE BY EXTRACTIVE DISTILLATION

the specification of which is attached hereto unless the following box is checked:

☒ was filed on **12 AUGUST 1998** as U.S. Application No. _____ or PCT International Application No. **PCT/US98/16689** and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.			
U.S. Provisional Application No.		U.S. Filing Date	
60/6055,502		08/12/97	

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application No.	Filing Date	Status (patented, pending or abandoned)
POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:		

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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